Effect of Pressure on the Spontaneous and Stimulated Emission from GaAs*

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The spontaneous and stimulated emission from diodes of GaAs has been studied at room and liquid-nitrogen temperatures as a function of hydrostatic pressure up to 8 kbar. The displacement with pressure of the spontaneous emission peak is $+1.1\times10^{-5}$ eV/bar which agrees with the pressure coefficient of the energy gap in GaAs and of analogous energy gaps in group 4 and group 3–5 compounds. The constancy of the linewidth with pressure suggests that an electron distribution in the conduction band is not responsible for the linewidth. Changes with pressure in the energy and intensity of lower energy emission lines provide information on the nature of the electronic transitions involved. Mode spikes of stimulated emission change energy with pressure as the crystal dimensions and the refractive index decrease, and these changes have been correlated with subsidiary measurements of the pressure coefficient of the index found from interference fringes. Suggestions for further informative measurements on other materials are made.

INTRODUCTION

AFTER it had been shown by Mayburg[1] and by Keyes and Quist[1] that radiative recombination was of major importance in restoring thermal equilibrium in GaAs, several laboratories[2–4] reported line narrowing, cavity mode selection, and other evidence for stimulated emission and coherent oscillation in *p-n* junction diodes. Directionality effects have also been extensively discussed.[5] The details of the recombination seem to be in debate, however, since it is not known whether the transition involved is band-to-band,[2] involves Zn, Cd, or other impurity centers,[3,4] or whether the band tailing caused by the high impurity density makes the difference a semantic one. Likewise the mechanism producing the linewidth—*inter alia*, a distribution of states in conduction or valence bands, thermal broadening, or a distribution of lattice defects and/or chemical impurities leading to a superposition of "separate" lines—is not established. Some of the details of mode selection appear to be understood. For example, in Fabry-Perot structures the separation between adjacent modes[6] appears to obey simple interference laws. On the other hand, the switching of modes with current level and with time in long pulses of stimulated emission seems to be much less understood.

This paper reports measurements of the spontaneous and stimulated emission as a function of hydrostatic pressure at liquid-nitrogen temperature and of the spontaneous emission at room temperature.[7] The displacement with pressure of the spontaneous emission peak is precisely determined and compared with the pressure coefficient of the band gap from optical absorption measurements. The linewidth, line shape, line intensity, and the emission intensity versus current characteristic have been studied. Changes in the cavity modes in stimulated operation have been extensively measured and analyzed using the known values for GaAs of compressibility, refractive index versus wavelength, and pressure dependence of refractive index. Subsidiary, lower energy lines[8] in the spontaneous emission spectrum have been examined in two diodes, and some conclusions regarding their origin have been possible.

EXPERIMENTAL TECHNIQUES

We have measured one diode from Lincoln Laboratory showing spontaneous emission, and several diodes from IBM Corporation showing both spontaneous and stimulated emission. The IBM diodes were diffused junctions doped with tellurium to a density of a few times 10^{17} per cc, and counterdoped with zinc. The Lincoln diode was formed by counterdoping with zinc *n*-type material not purposely doped with any impurity.

For the room-temperature measurements, the diode was mounted on a two-terminal electrical high-pressure plug immersed in liquid pentane in an optical high-pressure vessel of conventional design.[9] The geometry was such that the emitted radiation was directed through the half-inch thick sapphire window of the optical plug[9] opposite the electrical one. Adequate resolution for the spontaneous emission measurements (a spectral slit width $\Delta h\nu$ in the range of 0.04 to 0.006 eV) was provided by a 60° glass prism mounted in a

* Work supported in part by the U. S. Office of Naval Research.

[1] S. Mayburg, post-deadline paper, Baltimore American Physical Society meeting, March 1962; R. J. Keyes and T. M. Quist, Proc. IRE **50**, 1822 (1962); see also J. I. Pankove and M. Massoulie, Bull. Am. Phys. Soc. **7**, 88 (1962), and J. I. Pankove and J. E. Berkeyheiser, Proc. IRE **50**, 1976 (1962).

[2] R. N. Hall, G. E. Fenner, J. D. Kinglsey, T. J. Soltys, and R. O. Carlson, Phys. Rev. Letters **9**, 366 (1962).

[3] M. I. Nathan, W. P. Dumke, G. Burns, F. H. Dill, Jr., and G. Lasher, Appl. Phys. Letters **1**, 62 (1962).

[4] T. M. Quist, R. J. Keyes, W. E. Krag, B. Lax, A. L. McWhorter, R. H. Rediker, and H. J. Zeiger, Appl. Phys. Letters **1**, 91 (1962).

[5] See Refs. 2 and 3; G. Burns, R. A. Laff, S. E. Blum, F. H. Dill, Jr., and M. I. Nathan, IBM J. Res. Develop. **7**, 62 (1963); R. A. Laff, W. P. Dumke, F. H. Dill, Jr., and G. Burns, *ibid.* **7**, 63 (1963).

[6] J. D. Kingsley and G. E. Fenner, Bull. Am. Phys. Soc. **8**, 87 (1963); G. Burns, M. I. Nathan, B. A. Jenkins, and G. D. Pettit, *ibid.* **8**, 88 (1963).

[7] J. Feinleib, S. Groves, W. Paul, and R. Zallen, Bull. Am. Phys. Soc. **8**, 201 (1963).

[8] See Progress Report, Lincoln Laboratory, MIT, No. 2, 9 (1962) for a description of these lines and earlier observations of similar structure. Also, M. I. Nathan (private communication).

[9] D. Langer and D. M. Warschauer, Rev. Sci. Instr. **32**, 32 (1961).

Perkin-Elmer monochromator. The detector was an RCA 7102 photomultiplier cooled with dry ice. The radiation was chopped at 13 cps, phase-detected, amplified, and the signal recorded on a Leeds and Northrop type G recorder.

For the low-temperature measurements, using gaseous helium as pressure fluid, a second pressure vessel was wholly immersed in liquid nitrogen in a stainless steel dewar. The diode was mounted on a combination electrical and optical plug in which a central sapphire window was encircled by electrical lead-in wires. The radiation, emitted through the sapphire window, was conveyed via glass fiber optics to the source position of a Perkin-Elmer model 12G grating spectrometer. Since the spectra under study were confined to a narrow band, no foreprism or filter was needed to eliminate other orders. Possible distortion of the measured emission spectrum by the introduction of additional spectral selectivity was thus avoided. The grating was ruled at 1200 lines per mm, blazed at 7500 Å, and used in first order. In the range of interest, 8000 to 9000 Å (or 1.38 to 1.55 eV), spectral slit widths down to 2 Å (or 0.0004 eV) were obtainable. This was just enough resolution to allow observation of separate modes of oscillation in stimulated emission. The detector was again the cooled RCA 7102 photomultiplier. For dc injection currents up to 50 mA, the electronics was identical with that already briefly mentioned.

The measurements of stimulated emission spectra from the IBM diodes required high-current short-duration pulses. A coincidence detection circuit was employed which permitted direct linear response recording of the pulsed spectra. This useful, yet simple, circuit will be described in the next section since it appears that it has not been widely applied elsewhere.

Pressures up to 8 kbar were measured by manganin gauges, calibrated by observing the freezing pressure of mercury at 0°C, using the recent redetermination of this pressure of 7566 bars.[10]

DETECTION OF PULSED SPECTRA

The high-current pulses required for stimulated emission were obtained from an S.K.L. pulser, which discharged a coaxial cable through the GaAs diode and a series resistor, at a 70 cps repetition rate. The cable, charged from an external 2500 V power supply, provided pulses of up to 10 A of 300 nsec duration.

The photomultiplier output pulses were recorded by means of a coincidence gate circuit. Continuous recording is not only more convenient than a point-by-point method but is more likely to display fine structure in the spectral distribution. Among the basic requirements of such a detection system are (1) high sensitivity, so that the full resolution capabilities of the spectrometer may be utilized, (2) linear response for a wide range of signal amplitudes, and (3) rejection of spurious noise spikes during the long off-time between pulses. The system to be described is a simple transistor circuit meeting these requirements and possessing two additional advantages, viz., (1) the detector signal and the gate-opening signal are delayed relative to the primary exciting pulse, thus minimizing the pickup of transients; (2) the response time may be adjusted to allow averaging over many pulses, thus further reducing the noise.

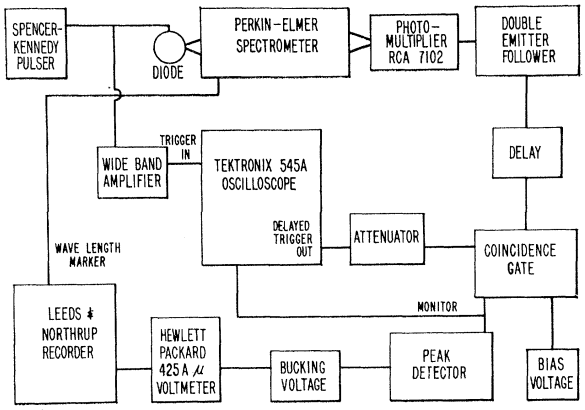

FIG. 1. Block diagram of the system.

Figure 1 shows a block diagram of the system. The photomultiplier signal is current amplified by a double emitter-follower configuration and delayed by about $\frac{1}{2}$ μsec before entering a coincidence circuit. The gate of this circuit is controlled by the variable delayed trigger of the Tektronix 545 A oscilloscope. The oscilloscope is triggered from the exciting pulse by tapping off a part of it with a high-impedance coaxial divider. When the photomultiplier signal and gate signal are synchronized by varying the oscilloscope delay, a heavily biased signal is passed into the peak recording detector integrator. A high-impedance dc microvoltmeter-amplifier then drives a recorder with a signal proportional to the charge on the integrator capacitor.

Figure 2 shows a circuit diagram of the special components of the detection system. The simple two transistor gate configuration has the following characteristics: The "on" resistance of the combination is much smaller than 50Ω so that it is well matched to 50-Ω coaxial cable; It has a fast dynamic response; the components do not need to be specially matched; It permits the signal to be superimposed on a large biasing pulse (see Fig. 3). This large biasing pulse at the gate output drives the diode well into a linear region of the I-V characteristic, producing a linear response to a wide range of signal amplitudes down to microvolt levels, and little output drift from the integrator due to change in operating point.

The relative widths and amplitudes of the gate pulses are shown in Fig. 3. The gate pulse may be taken directly from the oscilloscope Delayed Trigger or Gate Out. The latter would permit a gate of variable length.

[10] D. H. Newhall, L. H. Abbot, and R. A. Dunn, American Society of Mechanical Engineers, New York meeting, 1962 (unpublished).

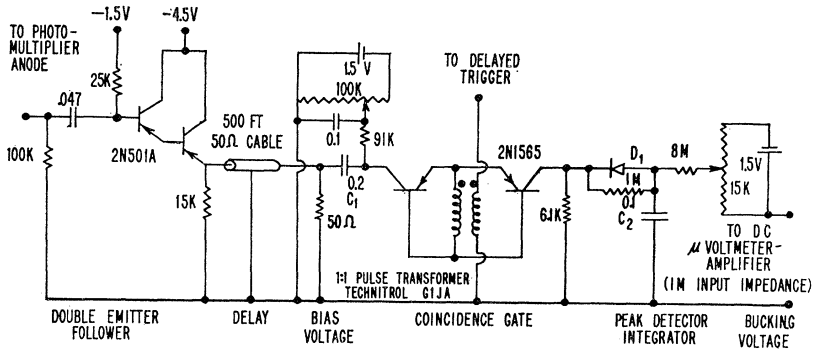

FIG. 2. Circuit diagram of special components of pulse-detection system.

The signal will not saturate the circuit as long as its amplitude is less than the difference between the gate pulse and the bias voltage. The minimum signal that can be detected will be determined by the short-term stability of the bias battery and bucking battery, as the signal amplitude in no way affects the gate operation. The large capacitor C_1 helps maintain the short-term stability of the bias voltage.

The large bias signal, by driving the integrator diode D_1 into a linear portion of its I–V characteristic, ensures that the integrating capacitor C_2 is charged proportional to the signal amplitude. The back biasing of D_1, when the gate is off, keeps C_2 charged to the signal peak. The bucking voltage is used to zero the system by removing the voltage contribution of the bias pulse. The discharge time constant of the integrator must also be optimized. Too slow a discharge time may lead to an incorrect signal record, unless the wavelength drive speed is correspondingly reduced. Too fast a discharge time (with respect to the response time of about 0.2 sec of the microvoltmeter-recorder combination) will lead to reduction in sensitivity. The best compromise, which also allows the integrator to average over many pulses even for low repetition rates, requires the discharge time constant to be about 0.1 sec.

Figure 4 shows a typical recording of a spectrum taken at 10 A, showing stimulated emission mode spikes.

RESULTS AND DISCUSSION—SPONTANEOUS EMISSION

(A) Energy of Main Line versus Pressure

Figure 5 shows the variation of the energy of the peak of the spontaneous emission line with pressure at 77 and 300°K. The peak of the line was taken as the mean of the energies corresponding to half-maximum intensity. Usually averages were taken over several lines at each pressure. The small variation in the zero-pressure energy of the line for different diodes at the same temperature has been found in previous investigations. Since the position of the peak usually depended on the current level through the diode to the lowest currents usable in our dc measurements, all the measurements during each pressure run were made at the same, low, closely regulated current level. The variation with pressure of the heat contact of the diode to the pentane bath is not supposed to have had any appreciable effect.

The (suitably averaged) peak energies are given by

$$\begin{aligned} &300°\text{K}: \; h\nu(\text{eV}) = 1.38 + (1.07 \pm 0.03) \times 10^{-5} P(\text{bars}), \\ &77°\text{K}: \; h\nu(\text{eV}) = 1.47 + (1.13 \pm 0.03) \times 10^{-5} P\ (\text{bars}). \end{aligned} \tag{1}$$

The closeness of the coefficients for all of the diodes at the two temperatures is to be noted. The coefficients can almost certainly be accepted as close to the pressure coefficient of the forbidden energy gap in GaAs, which had been previously determined as[11] 1.2×10^{-5} and[12] 0.96×10^{-5} eV/bar. The present coefficients are very close to those accepted for an analogous gap in germanium[13] (1.2–1.3×10^{-5} eV/bar), and other intermetallic compounds.[14] This supports a suggested empirical rule for the near equality of the pressure coefficients of corresponding energy separations in group 4 and group 3–5 semiconductors.[14]

However, the experiment provides no definitive in-

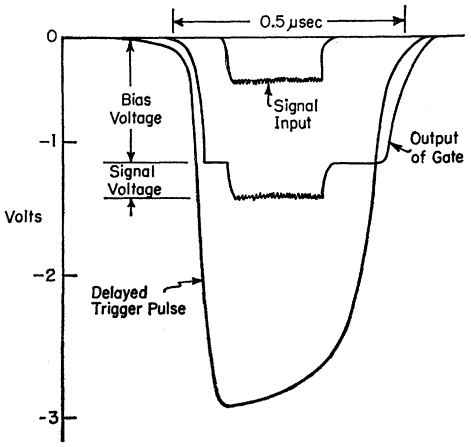

FIG. 3. Illustration of width and amplitudes of gate and signal pulses.

[11] W. Paul and D. M. Warschauer (unpublished measurements).
[12] A. L. Edwards, T. E. Slykhouse, and H. G. Drickamer, J. Phys. Chem. Solids **11**, 140 (1959).
[13] M. Cardona and W. Paul, J. Phys. Chem. Solids **17**, 138 (1960).
[14] W. Paul, Suppl. J. Appl. Phys. **32**, 2082 (1961).

formation on the exact mechanism of the transition giving the main spontaneous emission, since the pressure coefficient due to transitions between discrete levels near the band edges should be close to that for the main gap, and moreover, the present coefficient is more exact than any hitherto determined. Similarly, the equivalence of the coefficients for the diodes from IBM and Lincoln Laboratories suggests but does not establish that the transitions involved are the same.

(B) Linewidth of Main Line at Low Current Levels versus Pressure

A high resolution (grating) run at 77°K gave a linewidth at half-maximum intensity of about 0.03 eV which remained constant to within 2% to pressures of 8 kbar. No change in the shape of the line was observed. In lower resolution (prism) measurements at 300°K, the line width of about 0.04 eV remained constant to within 5% for the same pressure interval.

Since the line measured is determined both by the radiation emitted and absorption in the crystal, it seems that there is a zero or very small net pressure coefficient between the energy gap determining the absorption edge, and the energy gap determining the radiative emission, or else the absorption *in the material of the diode* produces little difference between the emitted and the measured spectrum.

These measurements may shed some light on the role of the conduction-band states in the emission. One possible transition mechanism is that electrons in a degenerate conduction-band distribution on the n side of the junction recombine with injected holes, either in the valence band or trapped on acceptor sites. A second possibility is that injected electrons forming a degenerate distribution in the conduction band on the p side recombine with holes present in equilibrium in the valence band or on acceptor sites. We shall take *as a model* a case where the linewidth is caused by a degenerate distribution in the conduction band emptying into a relatively discrete acceptor state; it seems likely that this will lead to the largest possible decrease with pressure of the linewidth, caused by a large increase with pressure of the conduction-band effective mass. Ignoring band tailing and nonparabolicity effects, we can calculate the effective mass change from

$$\frac{1}{m_n}\left(\frac{\partial m_n}{\partial P}\right)_T = -\frac{1}{E_g}\left(\frac{\partial E_g}{\partial P}\right)_T, \tag{2}$$

where $E_g \approx 1.4$ eV and $(\partial E_g/\partial P)_T \approx 1.1\times 10^{-5}$ eV/bar. The corresponding change in Fermi level can be translated into a decrease in linewidth at half-maximum intensity of about 5% in 8 kbar. This is outside the experimental limit of error of 2% of the 77°K measurement. This provides evidence, although not very strong evidence, that the main line-broadening mechanism is not the electron distribution in an unmodified conduction band, and suggests, even less strongly, that unmodified conduction-band states are not involved in the transitions.

On the other hand, pressure will increase the effective mass of the heavy mass holes in the valence band by

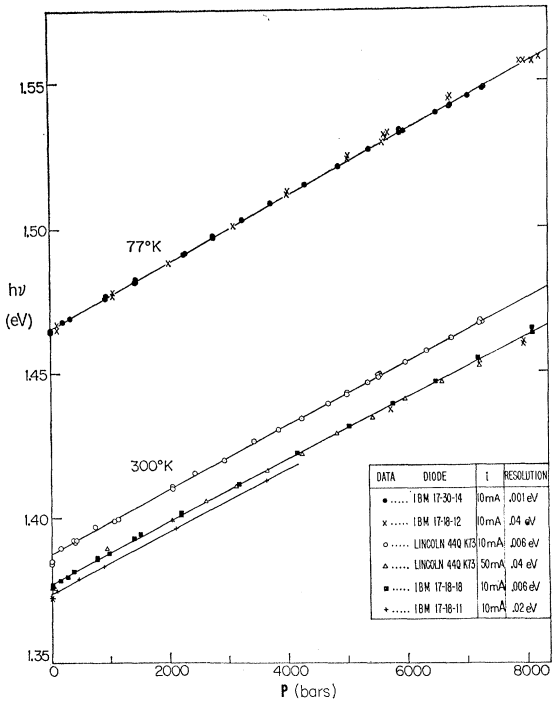

FIG. 5. Variation with pressure of the peak energy of the spontaneous emission line.

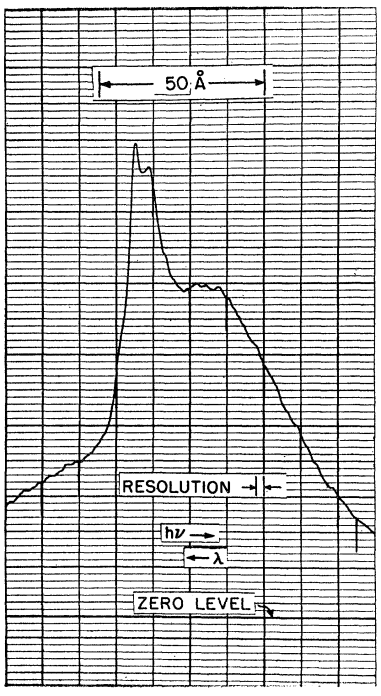

FIG. 4. Typical recording of spectrum of stimulated emission.

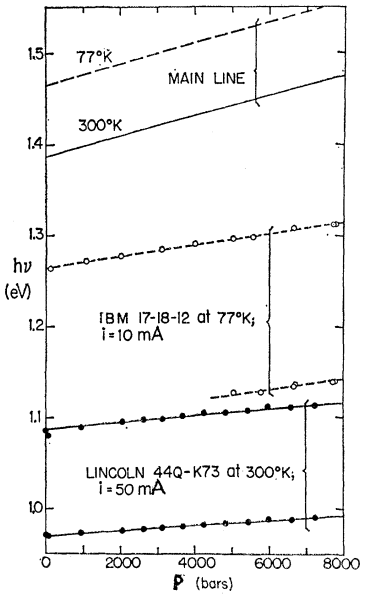

FIG. 6. Variation with pressure of the peak energy of subsidiary lines from the IBM and Lincoln diodes.

only 1% in 8 kbar, and the corresponding change in linewidth will be inside our limit of experimental error. There may be an effect of pressure on band tailing, but intuitively we expect that this will affect the low-energy threshold of the emission line without changing the width at half-maximum intensity. It seems unlikely that pressure will greatly affect any distribution in energy of the impurity states. In summary, although most of the transition mechanisms are consistent with the very small dependence on pressure of the linewidth, that involving the ordinary conduction band states, and where they are largely responsible for the linewidth, is shown to be unlikely.

(C) Intensity of Emission at Fixed Current versus Pressure

It is hard to interpret changes in measured emission intensity for the following reasons: the diode may shift slightly with pressure inside the pressure vessel; the sapphire windows distort; reflection losses at the semiconductor-fluid and fluid-sapphire interfaces change; the over-all sensitivity of the detection and measuring apparatus may change; and the spectral slit width of the spectrometer and the photomultiplier sensitivity vary with wavelength. The largest change in emitted intensity observed was 35% in 8 kbar.

(D) Emission Intensity-Current Characteristic versus Pressure

We found no effect of pressure on the shape of this characteristic, which is roughly linear in the range of currents used (3–50 mA).

(E) Current-Voltage Characteristic

The forward-bias current-voltage (I–V) characteristic for two diodes was measured versus pressure at room temperature. The results indicated that, for low current levels (μA)

$$e(\partial V/\partial P)_{I,T}=(\partial h\nu/\partial P)_T$$

to within 20%, where $h\nu$ refers to the peak energy of the main line.

(F) Spontaneous Lines at Lower Energies versus Pressure

Figure 6 shows the variation with pressure of the center of two broader, less intense, lower energy emission lines found in both IBM and Lincoln diodes. The Lincoln diode was measured at 300°K, the IBM one at 77°K. For the former, the energies of the peaks are

$$h\nu(\text{eV})=1.0+3\times10^{-6}P\ (\text{bars}),\qquad(3)$$

and

$$h\nu(\text{eV})=1.1+3\times10^{-6}P\ (\text{bars}),\qquad(4)$$

and for the latter,

$$h\nu(\text{eV})=1.1+6\times10^{-6}P\ (\text{bars}),\qquad(5)$$

and

$$h\nu(\text{eV})=1.3+6\times10^{-6}P\ (\text{bars}).\qquad(6)$$

Thus, all the coefficients are much smaller than for the main emission line. Measurements of the change with pressure of the ionization energies of gold impurities in germanium and silicon[15] have shown striking differences in the pressure coefficients of the separations of deep energy levels from the conduction and valence band edges. For example, an acceptor level almost exactly midway between the conduction and valence

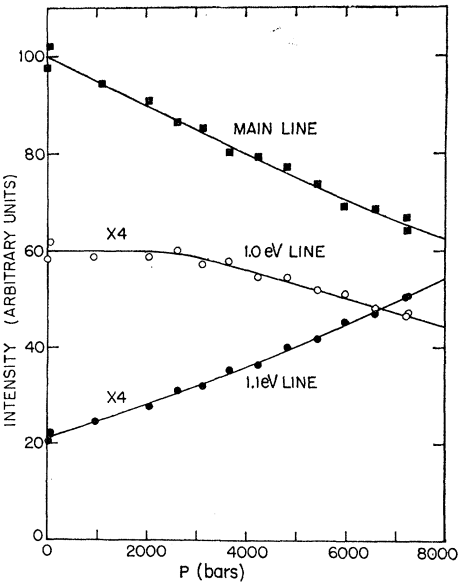

FIG. 7. Variation with pressure of the relative peak intensities of the main and two subsidiary lines from the Lincoln diode at 300°K.

[15] M. G. Holland and W. Paul, Phys. Rev. **128**, 43 (1962); M. I. Nathan and W. Paul, *ibid.* **128**, 38 (1962).

bands separates under pressure about four times faster from the conduction band than from the valence band. The small coefficients found here for energy differences that are three-quarters of the band gap would seem to suggest that the transitions do not involve conduction band states, i.e., the transitions are probably out of impurity levels about 0.1 and 0.4 eV below the conduction band into states near or in the valence band. On the other hand, absorption and photoconductivity studies at IBM[16] strongly suggest that in much of the material used for IBM diodes, transitions from the conduction band to levels about 0.4 and 0.1 eV above the valence band are more probable. This discrepancy has not yet been resolved.

The difference in coefficient between the IBM and Lincoln diodes is notable. It does not seem likely, particularly in view of the results for the main line, that this difference is due to the temperature difference. Thus, we presume that, although the two sets of spectra occur at the same energy, they actually correspond to different transitions. More measurements on a variety of diodes would seem to be advisable.

In Fig. 7 we show the variation in relative intensity with pressure of the main and the two subsidiary lines in the Lincoln diode at 300°K. Absolute variations of intensity are discounted for reasons already discussed. The changes are such that

$$I(1.0\text{ eV}):\ I(1.1\text{ eV}):\ I(1.4\text{ eV})=0.15:\ 0.05:1 \quad \text{at atmospheric pressure,} \tag{7}$$

and

$$I(1.0\text{ eV}):\ I(1.1\text{ eV}):\ I(1.4\text{ eV})=0.18:\ 0.21:1 \quad \text{at 8-kbar pressure.} \tag{8}$$

The subsidiary peaks are somewhat larger, relative to the main peak, at lower currents. We see that there is a change over in the line possessing the greater emitted intensity at the top pressures. Recall that the pressure coefficients of the two lines were equal. We have no explanation to offer for the intensity changes, which do however indicate new lines of experiment, that will be taken up in the final discussion. Finally, in this section, it should be mentioned that no hysteresis or time effects were observed in connection with these intensity changes.

RESULTS AND DISCUSSION—SPONTANEOUS AND STIMULATED EMISSION AT HIGH CURRENT LEVELS

One IBM diode exhibiting laser action was exhaustively studied at 77°K. The junction area in the diode was rectangular and the stimulated emission, which had a low threshold, was not very directional.[17] The cavity modes excited probably did not correspond to simple reflections in a Fabry-Perot type of geometry.

[16] A. E. Michel, W. J. Turner, and W. E. Reese, Bull. Am. Phys. Soc. 8, 215 (1963).
[17] M. I. Nathan (private communication).

TABLE I. Mode spikes in stimulated emission spectra.

Readings of mode peaks	Mode separation (Å)	Pressure coefficient ($\times 10^{-6}$ eV/bar)	Dimension $2t$ (cm)	Mean pressure (bars)
22	5.4	3.5	0.025	7100
11	3.2	4.3	0.043	7200
10	4.1	4.0	0.033	6100
10	3.6	4.4	0.038	1300
12	3.6	7.0	0.038	1300
7	2.7	3.5	0.050	5700
7	4.2	3.5	0.033	5700

(A) Narrowed Emission Line versus Pressure

At current densities of about 10 000 A-cm^{-2}, the emission line narrowed by about a factor of 3. This is much less than IBM has reported for similar structures, but this difference is of no consequence in our experiment. Between injection current densities of 100 A-cm^{-2} and 10 000 A-cm^{-2}, the energy of the peak of the line increased by about 0.01 eV. Similar shifts to higher energy with increasing current were also noted in the dc experiments and were first reported by Pankove.[18]

The pressure shift of the narrowed line is given by

$$h\nu(\text{eV})=1.48+(1.10\pm 0.03)\times 10^{-5}P\ (\text{bars}), \tag{9}$$

which is quite close to the value of 1.13×10^{-5} eV/bar obtained at low current densities. The comments and conclusions about the main line noted earlier apply here also.

(B) Linewidth of Narrowed Line versus Pressure

The degree of narrowing of the line with amplitude of the pulsed current was independent of pressure.

(C) Emission Intensity-Current Characteristic versus Pressure

The emission intensity-current characteristic became superlinear above about 4000 A-cm^{-2}, but there was no observable change in the characteristic, including the onset of superlinearity, with pressure.

(D) Mode Occurrence and Changes with Pressure

Above a threshold of approximately 4000 A-cm^{-2}, modes appeared on the low-energy side of the peak of the spontaneous line. By about 8000 A-cm^{-2}, these mode spikes built up to a level of about 30% of the background height. Figure 4 shows a recording of some of them, using the detection circuit described earlier. As we shall describe almost immediately, we believe we are able to deduce the separation in wavelength of modes belonging to the same geometrical path. These separations range from 6 down to 1.6 Å (the limit of resolution of our instrument is about this), with no apparent

[18] J. I. Pankove, Phys. Rev. Letters 9, 283 (1962).

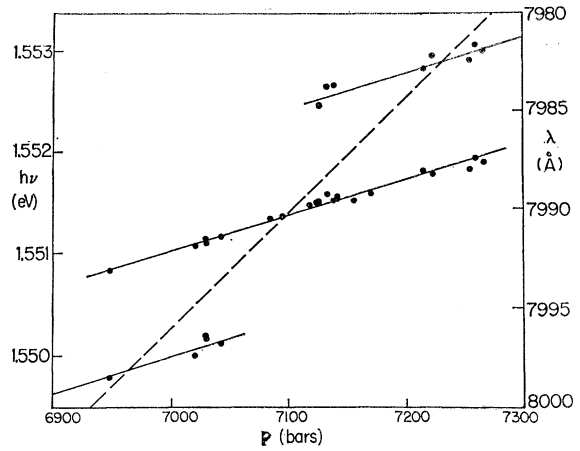

FIG. 8. Variation with pressure of the peak energy of three members of a family of stimulated emission modes. The dashed line has a slope of $+1.1\times10^{-5}$ eV/bar, the pressure coefficient of the main spontaneous-emission line.

regularity in the pattern. This is also illustrated in Table I which lists five different modes whose behavior under pressure was followed.

Two effects of pressure on the mode spikes are notable. (1) They shifted more slowly toward higher energy than the spontaneous emission background. A pressure increment both altered the position of the mode, and changed its intensity. (2) After a change of about 100 bars, the energy of coherent oscillation *switched* into a mode of different mode number m. This switch is caused by the relative displacement with pressure of the wavelength for a particular mode and the spontaneous emission line. The pressure increment over which one mode is "in sight" corresponds to a mode shift relative to the background line of about one mode separation. The first column of Table I lists the number of useful readings of mode peaks versus pressure for five separate modes. The second column gives the mode separation in angstroms. This was established best by observation of situations where two or more adjacent modes were simultaneously visible, and tiny pressure increments caused one to grow at the expense of the others. The third column lists the pressure shift of the mode peak, and we see that its value is

$$(\partial h\nu/\partial P)_{77^\circ\mathrm{K}}=4\times10^{-6}\ \mathrm{eV/bar}, \tag{10}$$

within a large error of $\pm1\times10^{-6}$ eV/bar. The best documented shift, displayed in Fig. 8, corresponds to 3.5×10^{-6} eV/bar. Stevenson, Axe, and Lankard[19] have also measured such pressure displacements of the mode peaks in similar IBM diodes at 77°K, obtaining a coefficient of 3×10^{-6} eV/bar. Fenner,[20] at General Electric, has found 2.8×10^{-6} eV/bar with an uncertainty of about 15%, from measurements at 195°K on the modes in a Fabry-Perot type of structure. The three measurements, therefore, agree within the large limit of error of our measurement.

An interesting side aspect of Table I is that the first listed mode appeared about halfway down the background line on the low-energy side, whereas all the others observed occurred just short of the peak of the background. It had the lowest threshold, about 1500 A-cm^{-2} as against 4000 A-cm^{-2} for the "top" modes. It has the largest mode separation, and above threshold slowly decreased in intensity relative to the background line. We speculate that it may correspond to a path geometry that for some obscure reason has a low threshold for resonance, but this is hardly convincing. The possibility that the whole background line is a composite of different transitions (say, between different defect levels) and that this particular one has a low threshold for stimulated emission cannot be excluded. The shift with pressure of the peaks of three members of this mode family is plotted in Fig. 8.

Independent of the geometrical paths followed by the light in the different modes, the condition for constructive interference should still be

$$2nt\bar{\nu}=m, \tag{11}$$

where n is the refractive index at wave number $\bar{\nu}$, m is an integer mode index, and $2t$ is the length of some unspecified path in the crystal. From Eq. (11), we find

$$2t\Delta\bar{\nu}=\left(n+\bar{\nu}\frac{\partial n}{\partial\bar{\nu}}\right)^{-1}, \tag{12}$$

where $\Delta\bar{\nu}$ is the wave number separation of adjacent modes corresponding to the path of length $2t$. The quantity on the right-hand side of Eq. (12) has been evaluated as 0.19 near 1.47 eV, at 77°K, by careful measurements on diodes with Fabry-Perot structures.[6,7] This leads to the values for $2t$ listed in the fourth column of Table I, which are to be compared with the cross-sectional measurements of the junction of 0.6 and 0.2 mm. The magnitudes of $2t$ look small, but may be explained if only a part of the junction is active.

From Eq. (11) we find, for the pressure coefficient of the energy of the mode peak,

$$-\left(\frac{\partial\ln h\nu}{\partial P}\right)_T=\frac{1}{1+(\bar{\nu}/n)(\partial n/\partial\bar{\nu})}\left(\frac{\partial\ln nt}{\partial P}\right)_T. \tag{13}$$

The linear compressibility of GaAs can be estimated from measurements of the ultrasonic velocities[21] as

$$(\partial\ln t/\partial P)_T=-0.44\times10^{-6}\ \mathrm{bar}^{-1}. \tag{14}$$

The pressure coefficient of the refractive index has recently been determined in our laboratory by DeMeis[22] from changes in the interference fringe pattern of a thin single-crystal film. Unfortunately, the experiments were confined to room temperature, since we do not have

[19] M. J. Stevenson, J. D. Axe, and J. R. Lankard, Bull. Am. Phys. Soc. 8, 310 (1963).
[20] G. E. Fenner (private communication).
[21] T. B. Bateman, H. J. McSkimin, and J. M. Whelan, J. Appl. Phys. 30, 544 (1959).
[22] M. DeMeis and W. Paul (to be published).

available a transmission pressure vessel for 77°K. DeMeis finds that the pressure coefficient is very dependent on the energy close to the absorption edge. Thus, although the long-wavelength (5 μ) pressure coefficent $(\partial \ln n/\partial P)_T$ is -0.7×10^{-6} bar^{-1}, that at 0.898 μ (1.38 eV) has increased to -2.3×10^{-6} bar^{-1}. The coefficient required in Eq. (13) is for 77°K, for the mean pressure of the mode shift experiment, and at the mean energy of the mode.

We have, therefore, estimated the coefficient $(\partial \ln n/\partial P)_{77°K}$ near zero pressure by determining it at the equivalent energy on the room-temperature curve near zero pressure. "Equivalent" here implies an energy translation that brings the n versus $h\nu$ curves for room and nitrogen temperatures into near-coincidence. Then,

$$(\partial \ln n/\partial P)_{77°K,P\to0}=-2.4\times10^{-6}\ \text{bar}^{-1}. \quad (15)$$

With $[n+\bar{\nu}(\partial n/\partial\bar{\nu})]^{-1}=0.19$, $n=3.59$, $h\nu=1.47$ eV, we compute from Eq. (13), (14), and (15)

$$(\partial h\nu/\partial P)_{77°K}=2.8\times10^{-6}\ \text{eV/bar}. \quad (16)$$

This coefficient is in fair agreement with our directly determined one, and in very good agreement with those of the G. E. and IBM workers.

Note that high pressures were used on most of our runs on the mode shifts. We have, therefore, also attempted to compute the coefficient near 6000 bars. From Eq. (13), and the discussion, it is clear that a different coefficient is to be expected, even though the experimental results listed in Table I have too large an individual error to display this difference. For this calculation, we first found $(\partial \ln n/\partial P)_{77°K}$ from the value of the equivalent energy on the room temperature, high-pressure curve. This gave

$$(\partial \ln n/\partial P)_{77°K,6000\ \text{bars}}=-(3\ \text{to}\ 3.5)\times10^{-6}\ \text{bar}^{-1}, \quad (17)$$

depending on an awkward extrapolation from 1.4 to 1.47 eV. An adjusted value of $[1+(\bar{\nu}/n)(\partial n/\partial\bar{\nu})]^{-1}$ was found by multiplying its value at 77°K, 1.47 eV, zero pressure, by the ratio

$$\frac{[1+(\bar{\nu}/n)(\partial n/\partial\bar{\nu})]^{-1}\ \text{for 300°K, 6000 bars, } E-\Delta}{[1+(\bar{\nu}/n)(\partial n/\partial\bar{\nu})]^{-1}\ \text{for 300°K, 0 bars, } 1.47-\Delta},$$

where E is the mode energy at 6000 bars, 77°K, and Δ is the shift in energy required to bring the 77°K and room temperature curves of n versus $h\nu$ into near-coincidence. Then

$$[1+(\bar{\nu}/n)\partial n/\partial\bar{\nu}]^{-1}=0.78. \quad (18)$$

With $E=h\nu=1.54$ eV, we find

$$(\partial h\nu/\partial P)_{77°K}=4.1\ \text{to}\ 4.7\times10^{-6}\ \text{eV/bar}. \quad (19)$$

Thus, higher mode shifts are predicted at higher pressures, and therefore higher energies, and this seems to be in accord with the data recorded. We conclude that the mode shifts can be explained in terms of changes in the dimension and refractive index of the GaAs. It is of interest that Burns and Nathan[23] have reported shifts with temperature of modes of 0.46±0.1 Å/°K. Equation (13) in T instead of P describes these shifts, and use of measured temperature changes of the refractive index at 77°K near the mode energy,[24] the thermal expansion coefficient, and Eq. (12) predicts a shift of about 0.9 Å/°K.

The threshold current for mode occurrence was not as sharply defined in this diode as in those recently reported. It appeared that an upper limit for change of the threshold current was about 20% in 8 kbar.

CONCLUSIONS

These measurements determine with very high precision the pressure coefficient of the energy of the radiative emission peak in GaAs and show that this is very close to the coefficient of the energy gap in GaAs and of analogous energy gaps in other group 4 and group 3–5 semiconductors. The constancy of linewidth with pressure tends to eliminate an electron distribution in a degenerate conduction band as the source of the linewidth. Differences in the pressure coefficients of subsidiary, lower energy lines in diodes from two sources indicate that the transitions involved are different. The smallness of these coefficients is interpreted to imply that the transitions are out of high-lying impurity levels into levels close to or in the valence band. Variations in the relative intensity of the subsidiary and main lines are notable.

Mode spikes of stimulated emission change energy under pressure as the refractive index and crystal dimensions change. The relative shift of the spontaneous line and the energy for a particular mode causes switches of the energy of coherent oscillation from one mode to another.

It is doubtful if much more information will be gained from a study of the modes. However, an accurate determination of their pressure coefficient in a Fabry-Perot type of structure might demonstrate a change of the coefficient with pressure, which would present an interesting test of the validity of our present method of correlating theory with experiment.

The pressure dependence of the emission lines would give another measure of the energy gap changes in other semiconductors of this family. In GaSb and in some GaAs-GaP alloys the smallest gap is direct at low pressures and indirect at high pressures. The intensity of the emission should change with pressure as the conduction band carriers change their k vector, or alternatively, as electrons bound to imperfections with energy levels just below the conduction band change the composition of their wave function. Lower energy

[23] G. Burns and M. I. Nathan, Proc. I.E.E.E. **51**, 471 (1963); M. I. Nathan (private communication) for value quoted.
[24] D. T. Marple (private communication).

lines will be similarly affected. Since the pressure coefficients of the different parts of these band structures are well known,[14] quantitative data on wave functions could be found. Similar pressure measurements should also be useful in confirming the indirect character of the band gap in GaP, in investigating the mechanism of red emission in this compound, and in determining the energies of higher minima, which are at present uncertain.[14] Extensions to the 2–6 compounds are certainly possible; it is to be noted that experiments of this sort have already been reported by Langer.[25]

[25] D. Langer, in *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Publishing House of the Czechoslovak Academy of Sciences, Prague, 1961), p. 1042.

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de Haas–van Alphen Effect in Zirconium*

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The de Haas–van Alphen effect has been observed in single crystals of zirconium in pulsed magnetic fields up to 190 kG. A rotating coil device has been used to study the periods of the oscillations as a function of magnetic field direction in the (00·1), (10·0), and (1$\bar{1}$·0) planes of the hexagonal crystals. Five separate oscillatory terms have been observed with periods ranging in value from 2.0 to 3.4×10^{-8}G^{-1}. The data, in general, do not agree with the Fermi surface predicted by the nearly free electron model.

I. INTRODUCTION

THE diamagnetic susceptibility of pure metal single crystals exhibits an oscillatory behavior at low temperatures known as the de Haas–van Alphen (dHvA) effect. These oscillations are periodic in the reciprocal magnetic field and are important in the study of the electronic structure of metals due to their relation to the Fermi surface of the metal. The period P is related to an extremal cross-sectional area of the Fermi surface normal to the magnetic field direction by the relation[1] $P=4\pi^2e/chA=9.546\times10^7/A$, when P is expressed in G^{-1} and A is the extremal area in $\mathbf{k}$ space in units of cm^{-2}. Studies of the dHvA effect have proved to be extremely valuable in mapping the Fermi surface of the noble metals[2] and many other low valence metals (e.g., Mg,[3] Zn,[4] Al,[5] Pb [6]). In contrast, there have been few detailed measurements relating to the Fermi surface of transition metals. We report here on a systematic pulsed-magnetic-field study of the dHvA effect in zirconium.

II. APPARATUS

The pulsed-magnetic-field apparatus used in the present experiments has in principle been described elsewhere.[7] Magnetic fields up to 190 kG are produced impulsively by discharging an 1800-μF capacitor bank charged to 3000 V through a copper wire-wound solenoid cooled to liquid-nitrogen temperature. The field rises approximately sinusoidally to a peak value in 4.44 msec,[8] and 1 msec later the magnet is shorted, allowing the field to decay exponentially with an L/R time constant of 16 msec. To insure field uniformity in the central region, the solenoid is fitted with trimmer coils which maintain field homogeneity to better than one part in 10^4 over a distance of 10 mm. A stainless steel liquid helium Dewar with 1.27-cm outer tail diameter fits into the solenoid and provides a 1.09-cm-diam working space for the rotating coil apparatus. (The rotating coil device has been described in detail in a separate publication.[9]) The detection coil containing the

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[3] W. L. Gordon, A. S. Joseph, and T. G. Eck, in *The Fermi Surface* (John Wiley & Sons, Inc., New York, 1960), p. 84; M. G. Priestley, in *Proceedings of the Seventh International Conference on Low Temperature Physics*, edited by G. M. Graham and A. C. Hollis Hallet (The University of Toronto Press, Toronto, 1960), p. 230.
[4] A. S. Joseph and W. L. Gordon, Phys. Rev. **126**, 489 (1962).
[5] E. M. Gunnerson, Phil. Trans. Roy. Soc. London **A249**, 299 (1957); M. G. Priestley, Phil. Mag. **7**, 1205 (1962).
[6] A. V. Gold, Phil. Trans. Roy. Soc. London **A251**, 85 (1958).
[7] D. Shoenberg, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (Interscience Publishers, Inc., New York, 1957), p. 226.
[8] In the final measurements on zirconium, the capacitor banks were enlarged to 5400 μF, giving a rise time of $\approx$7 msec.